

# Effective three-band model for double perovskites

P. Petrone and A. A. Aligia

*Comisión Nacional de Energía Atómica, Centro Atómico Bariloche and Instituto Balseiro, 8400 S.C. de Bariloche, Argentina.*

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We start from a six-band model describing the transition-metal  $t_{2g}$  orbitals of half-metallic double perovskite systems, such as  $\text{Sr}_2\text{FeMoO}_6$ , in which only one of the transition metal ions (Fe) contains important intratomic repulsion  $U_{Fe}$ . By eliminating the Mo orbitals using a low-energy reduction similar to that used in the cuprates, we construct a Hamiltonian which contains only effective  $t_{2g}$  Fe orbitals. This allows to treat exactly  $U_{Fe}$  and most of the Fe-Mo hopping. As an application, we treat the effective Hamiltonian in the slave-boson mean-field approximation and calculate the position of the metal-insulator transition and other quantities as a function of pressure or on-site energy difference.

## I. INTRODUCTION

In the simple perovskites of formula unit  $\text{AMO}_3$ , the transition metal atoms  $M$  form a simple cubic lattice. In the double perovskites  $\text{A}_2\text{MM}'\text{O}_6$ , this lattice is subdivided into two interpenetrating f.c.c. sublattices, in such a way that the nearest transition metal  $M'$  lies in the sublattice occupied by  $M$  and vice versa.  $A$  is an alkaline earth. Recently, the interest on these systems has considerably increased after the finding of low-field colossal magnetoresistance (CMR) in  $\text{Sr}_2\text{FeMoO}_6$ , which remains significant at room temperature.<sup>1</sup> The system is a half metallic ferromagnet with a Curie temperature near 450K. The mechanism leading to CMR at low fields is believed to be intergrain carrier scattering between regions of different orientation of magnetization, which is reduced under an applied magnetic field. Other double perovskites systems which were studied include  $\text{Ba}_2\text{FeMoO}_6$ ,<sup>2</sup>  $\text{Sr}_2\text{FeReO}_6$ ,<sup>3</sup>  $\text{Sr}_2\text{FeWO}_6$ ,<sup>4</sup> and the alloy  $\text{Sr}_2\text{FeMo}_{1-x}\text{W}_x\text{O}_6$ .<sup>5</sup>  $\text{Sr}_2\text{FeWO}_6$  is an insulating antiferromagnetic system, and the research on this alloy monitors the transition from metallic itinerant ferromagnetism in  $\text{Sr}_2\text{FeMoO}_6$  to localized-electron antiferromagnetism in  $\text{Sr}_2\text{FeWO}_6$ . Also, substitution of Fe by Co or Mn renders  $\text{Sr}_2\text{FeMoO}_6$  antiferromagnetic and insulating.<sup>6</sup> Ordinary ab initio calculations fail to explain the electronic structure of  $\text{Sr}_2\text{FeWO}_6$ , obtaining a metallic ferromagnetic ground state.<sup>7</sup> This result changes if the phenomenological method called LDA+U is used.<sup>7</sup>

An issue related with the electronic structure of  $\text{Sr}_2\text{FeMoO}_6$  which is not settled yet is the valence of the transition metal ions. This is in principle related with the metallic or insulating character, since in an ionic picture with oxidation states  $\text{O}^{-2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Fe}^{+2}$  and a closed shell  $\text{Mo}^{+6}$ , one might expect that the strong Coulomb repulsion at Fe sites  $U_{Fe}$  brings the system close to a Mott transition.<sup>8</sup> While the Mo-3d chemical shift observed in optical experiments is practically identical to that of  $\text{MoO}_3$  (indicating formal valence  $\text{Mo}^{+6}$ ), the formal valence of Fe seems to be +3.<sup>9</sup> This apparently contradictory result is interpreted by the authors as an indication of covalency. Mössbauer experiments are inter-

preted also as indicating covalency.<sup>10</sup> Nevertheless, as we shall see, even assuming that all O ions are  $\text{O}^{-2}$ , there is a certain degree of covalency in the insulating state. Results from neutron diffraction experiments obtain magnetic moments  $\mu_{Fe} = 4.1 \pm 0.1 \mu_B$  and  $\mu_{Mo} = 0 \pm 0.1 \mu_B$ .<sup>11</sup> These values are consistent with an insulating state, suggesting that  $\text{Sr}_2\text{FeMoO}_6$  is near a metal-insulator transition.

The metal-insulator transition has been studied theoretically applying the slave-boson mean-field approximation (SBMFA) to a six-band model containing the relevant Mo and Fe  $t_{2g}$  orbitals, neglecting the hopping between Mo ions and taking a simplified density of states<sup>8</sup>. The SBMFA permits to treat  $U_{Fe} \simeq 7\text{eV}$  in a way equivalent to the Gutzwiller approximation.<sup>12</sup>

The aim of the present work is to derive an effective 3-band Hamiltonian, eliminating the Mo sites by a suitable low-energy reduction procedure. This procedure has been successfully used in the cuprates. After the original proposal of Zhang and Rice<sup>13</sup> that in spite of Cu-O covalency, the low energy physics of the superconducting cuprates can be described by a one-band model, several systematic studies have derived the different terms of this model and used it successfully to calculate several properties.<sup>14–21</sup> The advantages of the effective model is that it has a smaller Hilbert space in numerical diagonalizations of finite systems and that the largest interaction in the problem  $U_{Fe}$  (or the on-site repulsion at Cu in the case of cuprates) is treated exactly inside an effective cell. As a consequence, one expects that approximate treatments give better results when applied to the effective Hamiltonian rather than the original one. This is the case of the SBMFA applied to calculate the metal-insulator transition in the cuprates: the results are significantly improved when applied to the effective one-band model.<sup>16</sup>

Our resulting low-energy Hamiltonian contains only effective Fe sites with a reduced effective Coulomb repulsion ( $U < 2.8\text{eV}$  for  $\text{Sr}_2\text{FeMoO}_6$ ). It can be described as a one-band model containing three pseudospin or “color” components describing the  $xy$ ,  $yz$ , and  $zx$   $t_{2g}$  orbitals of the 3d or 4d shell. For the simpler two-color version

FIG. 1. Scheme of the effective hopping between nearest  $d_{xy}$  orbitals through intermediate O  $2p$  orbitals.

This is already an effective Hamiltonian in which the O atoms, which lie in between any two transition metal atoms, were eliminated. This procedure can be done using perturbation theory<sup>8,24</sup> if late 3d transition metal atoms (like Ni or Cu) are not involved. Due to the symmetry of the intermediate O orbitals, one realizes that hopping Fe-Mo  $t_{FM}$  is two dimensional: it is nonzero only between  $\sigma$  orbitals lying on the plane  $\sigma$  (see Figure 1). Thus, it conserves color. We take  $U_{Fe} = 7$  eV from spectroscopic studies.<sup>25</sup> Here we derive the other parameters of the model for  $\text{Sr}_2\text{FeMoO}_6$  by fitting *ab initio* results for the  $t_{2g}$  bands obtained previously,<sup>8</sup> to the corresponding result of Eq. (1) in the Hartree-Fock approximation. In this approximation  $U_{Fe}$  is taken as zero and  $\varepsilon_{Fe}$  is replaced by  $\varepsilon_{Fe}^{HF} = \varepsilon_{Fe} + \frac{2}{3}U_{Fe}n_{Fe}^{HF}$ , where  $n_{Fe}^{HF}/3$  is the expectation value of  $f_{i\sigma}^\dagger f_{i\sigma}$  (independent of  $i$  and  $\sigma$ ) in the Hartree-Fock approximation. We have adjusted the two eigenvalues for wave vector  $\Gamma = \mathbf{0}$ , and the other two for wave vector  $L = (\pi/a, \pi/a, \pi/a)$ , where  $a$  is the lattice parameter of the f.c.c. structure. This fitting gives the values of:  $\varepsilon_{Fe}^{HF}$ ,  $\varepsilon_{Mo}$ ,  $t_{FM}$  and  $t_{MM}(\sigma, \sigma, \gamma_\sigma)$ , where  $\gamma_\sigma$  lies in the plane  $\sigma$  (see Fig. 2). The other two independent values of  $t_{MM}(\sigma, \sigma', \gamma)$  are smaller. For simplicity, their values are derived using the geometrical relations that correspond to direct Mo-Mo hybridization,<sup>26</sup> and taking the following relations for the components with different angular momentum projection of the hopping integrals:  $(dd\delta) = 0$ ,  $(dd\pi)/(dd\sigma) = -0.54$ .<sup>27</sup> The occupation  $n_{Fe}^{HF}$  was obtained from the resulting tight-binding dispersion, what allows us to derive a  $\varepsilon_{Fe}$  from  $\varepsilon_{Fe}^{HF}$ . We have repeated the procedure for several lattice parameters. Using the numerical derivative of the *ab initio* energy with respect to volume, we obtain the dependence of the parameters with pressure, as indicated in Table I. The most significant change with applied pressure is the increase in the magnitude of  $t_{FM}$ . In contrast,  $\varepsilon_{Mo} - \varepsilon_{Fe}$  decreases with applied pressure. Both effects

favor a metallic state by decreasing the probability of finding localized electrons at the Fe sites. Note that while  $\varepsilon_{Fe}$  lies  $\sim 2.5$  eV below  $\varepsilon_{Mo}$ ,  $\varepsilon_{Fe}^{HF}$  is close to  $\varepsilon_{Mo}$ . This is consistent with other *ab initio* calculations.<sup>1,7,28</sup> As a consequence,  $n_{Fe}^{HF} \sim 0.5$ . However this value is significantly increased, and the amount of covalency is reduced, when  $U_{Fe}$  is treated in a more realistic approximation.

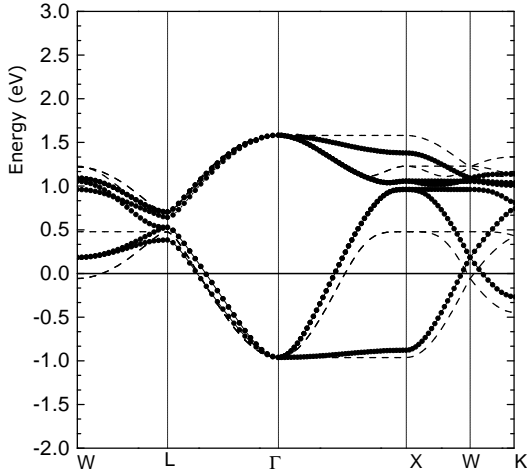


Fig. 2

FIG. 2. Calculated  $t_{2g}$  energy bands (full line and solid circles) and fitting using Eq. (1) in the Hartree-Fock approximation (dashed lines). The Fermi energy is at 0 eV. The wave vectors shown are: W =  $(\pi/a, 0, 2\pi/a)$ , L =  $(\pi/a, \pi/a, \pi/a)$ ,  $\Gamma = (0, 0, 0)$ , X =  $(0, 0, 2\pi/a)$ , and K =  $(3\pi/2a, 3\pi/2a, 0)$ .

$a(??)$	$P(\text{GPa})$	$t_{FM}(\text{eV})$	$t_{MM}(\text{eV})$	$\varepsilon_{Mo} - \varepsilon_{Fe}(\text{eV})$
16.51	-25.13	0.1517	0.0799	2.787
15.71	-24.95	0.1955	0.0956	2.713
15.31	-16.74	0.2459	0.1122	2.623
15.11	-9.14	0.2781	0.1222	2.555
14.91	-3.40	0.2960	0.1296	2.512
14.81	3.45	0.3150	0.1361	2.442
14.71	7.04	0.3242	0.1390	2.390
14.61	10.72	0.3338	0.1433	2.268
14.51	18.15	0.3510	0.1531	2.338

Table I - Pressure and parameters of Eq. (1) for differ-

ent lattice parameters, obtained fitting *ab initio* energies at  $\Gamma$  and L, with the results of Eq. (1) in the Hartree-Fock approximation.

### III. THE EFFECTIVE HAMILTONIAN

In this section, we derive a Hamiltonian containing only effective Fe sites, which describes the low-energy physics of  $\text{Sr}_2\text{FeMoO}_6$  or other double perovskites. The procedure is basically the same as the one used in the cuprates<sup>14–21</sup> and consists of the following steps: i) change of basis of Mo  $m_i$  orbitals to Wannier functions centered at the Fe sites, ii) exact diagonalization of the cell Hamiltonian  $H_i$  at each Fe site  $i$ , retaining the ground state for each number of particles. These states are mapped into the corresponding states of a Hamiltonian that contains only Fe  $t_{2g}$  states. iii) calculating the intercell hopping matrix elements  $(H - \sum_i H_i)$  in the restricted subspace of the cell ground states, and iv) inclusion of the excited states by perturbation theory.<sup>18,19</sup> We actually neglect the last step because these corrections are very small, ensuring the validity of the effective Hamiltonian.

#### A. Change of basis of Mo orbitals

The Mo Wannier orbitals  $\alpha_{i\sigma}$  centered at Fe site  $i$  are constructed Fourier-transforming the  $m_{j\sigma}$  in the plane  $\sigma$  at which the orbital  $\sigma$  lies, and then transforming the dependence on the two-dimensional wave vector back to real space:

$$\begin{aligned}
 \alpha_{i\sigma} &= \frac{1}{N_\sigma} \sum_{k,l} e^{ik \cdot (R_i - R_l)} m_{l,\sigma} \\
 &= \sum_{\Delta_\sigma} C_\sigma(\Delta_\sigma) m_{i+\Delta_\sigma,\sigma}, \\
 \text{with } C_\sigma(\Delta_\sigma) &= \frac{1}{N_\sigma} \sum_{k_\sigma} e^{-ik_\sigma \Delta_\sigma}
 \end{aligned} \tag{2}$$

where  $N_\sigma$  is the number of atoms lying in the plane  $\sigma$ ,  $k_\sigma$  are two-dimensional reciprocal lattice vectors parallel to the plane  $\sigma$ , and  $\Delta_\sigma$  are the vectors lying in the plane  $\sigma$  which connect an Fe site with all Mo sites in this plane. The vector  $\Delta_\sigma$  does not belong to the Bravais lattice. Performing the two-dimensional integral, one obtains:

$$C(\Delta_\sigma) = \frac{4}{\pi^2} \frac{(-1)^{n_x} - (-1)^{n_y}}{(n_y^2 - (n_x^2))}, \text{ with } \Delta_\sigma = \frac{a}{2}(n_x \hat{x} + n_y \hat{y}), \tag{3}$$

where  $n_x, n_y$  are two integers of opposite parity and  $\hat{x}, \hat{y}$  are the unit vectors of the plane  $\sigma$ .

Using the inverse of Eq. (2) and some algebra, the Hamiltonian in the new basis takes the form:

$$H = \sum_i H_i - \left( \sum_{i\sigma\mu_\sigma \neq 0} \widetilde{t_{FM}}(\sigma, \mu_\sigma) f_{i\sigma}^\dagger \alpha_{i+\mu_\sigma\sigma} + \sum_{i\sigma\sigma'\nu} \widetilde{t_{MM}}(\sigma, \sigma', \nu) \alpha_{i\sigma}^\dagger \alpha_{i+\nu\sigma'} + \text{H.c.} \right), \quad (4)$$

with

$$H_i = \varepsilon_{Fe} \sum_\sigma f_{i\sigma}^\dagger f_{i\sigma} + \varepsilon_{Mo} \sum_\sigma \alpha_{i\sigma}^\dagger \alpha_{i\sigma} + U_{Fe} \sum_{\sigma < \sigma'} f_{i,\sigma}^\dagger f_{i,\sigma} f_{i,\sigma'}^\dagger f_{i,\sigma'} + \sum_\sigma [\widetilde{t_{FM}}(\sigma, 0) f_{i\sigma}^\dagger \alpha_{i\sigma} + \text{H.c.}] \quad (5)$$

$\mu_\sigma$  and  $\nu$  are vectors of the f.c.c. Bravais lattice and the former lies in the plane  $\sigma$ . The change of basis has introduced hoppings at arbitrary distances, but as we shall show, they decay very rapidly with distance. This decay is different from those of similar hopping terms in the case of the cuprates due to the different nature of the Wannier orbitals. The hopping between Fe and new Mo orbitals at a distance  $\mu_\sigma = \frac{a}{2}(n_x \hat{x} + n_y \hat{y})$  (where now  $n_x, n_y$  are two integers of the same parity) is:

$$\frac{\widetilde{t_{FM}}(\sigma, \mu_\sigma)}{t_{FM}} = \sum_{\sigma\delta_\sigma} C_\sigma(\mu_\sigma - \delta_\sigma) = \frac{16}{\pi^2} \frac{(-1)^{n_x}}{(n_x^2 - n_y^2)^2 - 2(n_x^2 + n_y^2) + 1}. \quad (6)$$

The weakest decay is along the diagonal direction  $n_x = n_y$ . For  $n_x = n_y = 0$ ,  $\widetilde{t_{FM}}(\sigma, 0)/t_{FM} = 16/\pi^2 \simeq 1.62$ . As a consequence most of the original hopping terms are included in  $\sum_i H_i$ , that will be solved exactly. For the hopping between different Mo  $\alpha_i$  orbitals we have to distinguish two cases:

$$\widetilde{t_{MM}}(\sigma, \sigma', \nu) = \begin{cases} t_{MM}(\sigma, \sigma, \nu) & \sigma = \sigma' \\ \sum_\eta t_{MM}(\sigma, \sigma', \nu - \eta) S(\eta) & \sigma \neq \sigma' \end{cases}, \quad (7)$$

where

$$S(\eta) = \sum_{\Delta_\sigma} C_\sigma(\Delta_\sigma) C_{\sigma'}(\Delta_\sigma + \eta), \quad (8)$$

and the sum over  $\Delta_\sigma$  is restricted to vectors such that  $\Delta_\sigma + \eta$  lies in the  $\sigma'$  plane. This sum is evaluated in Appendix A. The sum over  $\eta$  in Eq. (7) is restricted to Bravais lattice vectors such that  $\nu - \eta$  are NN in the f.c.c. lattice, because otherwise  $t_{MM}(\sigma, \sigma', \nu - \eta)$  vanishes. Also, due to symmetry arguments, if  $\sigma \neq \sigma'$  then  $t_{MM}(\sigma, \sigma', \nu) = 0$  unless  $\nu$  lies in the plane perpendicular to both  $\sigma$  and  $\sigma'$ . The color-conserving hopping  $\widetilde{t_{MM}}(\sigma, \sigma, \nu)$  retains the same form as in the original Mo basis with a rigid shift in the positions of the orbitals (from Mo to Fe positions). Some values

of these hoppings for the experimental lattice parameter are:  $t_{FM}(\sigma, 0) = 0.51$  eV,  $\widetilde{t_{FM}}(\sigma, \delta_\sigma) = 0.17$  eV,  $\widetilde{t_{MM}}(\sigma, \sigma, \gamma_\sigma) = 0.14$  eV where  $\gamma_\sigma$  connects nearest neighbor ions in the f.c.c. lattice and lies in the plane  $\sigma$ . For larger distances,  $\widetilde{t_{MM}}$  is at most of order 0.01 eV.

## B. Diagonalization of the cell Hamiltonian

$H_i$  can be diagonalized exactly in each subspace of definite number of electrons and of states which transform under the point group operations as a basis function of some irreducible representation. The ground state of the most relevant subspaces is mapped into the corresponding state of a monatomic f.c.c. lattice with  $t_{2g}$  orbitals. For example, in the subspace of one electron and wave functions transforming like  $\sigma$  ( $xy$ ,  $yz$ , or  $zx$ ), the ground state has the form:

$$|i1\sigma\rangle = (A_1 f_{i\sigma}^\dagger + B_1 \alpha_{i\sigma}^\dagger) |0\rangle, \quad (9)$$

and is mapped onto the state  $c_{i\sigma}^\dagger |0\rangle$  of the effective monatomic Hamiltonian  $H_{eff}$ . Similarly, the ground state for two particles has the form

$$|i2\sigma\sigma'\rangle = [A_2 \alpha_{i\sigma}^\dagger \alpha_{i\sigma'}^\dagger + B_2 f_{i\sigma}^\dagger f_{i\sigma'}^\dagger + C_2 (\alpha_{i\sigma}^\dagger f_{i\sigma'}^\dagger + f_{i\sigma}^\dagger \alpha_{i\sigma'}^\dagger)] |0\rangle, \quad (10)$$

and is mapped onto the state  $c_{i\sigma}^\dagger c_{i\sigma'}^\dagger |0\rangle$ . In the present work and since we are interested in occupations near one electron per lattice site, we disregard the states with three electrons in the cell. This does not modify the results for the metal-insulator transition presented in the next section. The inclusion of three-particle states is straightforward but complicates the notation and introduces several new terms in  $H_{eff}$ . For  $\text{Sr}_2\text{FeMoO}_6$  at the experimentally observed lattice constant we obtain  $E_1 = \varepsilon_{Fe} - 0.092\text{eV}$  and  $E_2 = 2\varepsilon_{Fe} + 2.442\text{eV}$ , where  $E_n$  is the on-site energy in  $H_{eff}$ , and the effective Coulomb repulsion is  $U = E_2 + E_0 - 2E_1 = 2.625\text{eV}$ . This strong reduction with respect to  $U_{Fe} = 7\text{eV}$  is due to the fact that  $|i2\sigma\sigma'\rangle$  is dominated by the last term in Eq. (10). In other words, it is energetically more favorable to occupy one Fe orbital and one Wannier Mo orbital at that site, due to the large intratomic repulsion in Fe.

## C. The intersite terms

The hopping terms  $H - \sum_i H_i$ , calculated in the restricted basis defined above, lead to effective hopping terms in  $H_{eff}$ . In addition to the dependence on the lattice vector and orbitals involved, the effective hopping depends on the occupation of the two sites involved. We denote by  $t_i$  ( $i = 1$  to 3), the matrix elements which correspond to the following transitions: 1)  $|i0, j1\sigma\rangle \longleftrightarrow |i1\sigma', j0\rangle$  2)  $|i1\sigma', j1\sigma\rangle \longleftrightarrow |i0, j2\sigma\sigma'\rangle$  3)

$|i1\sigma_1, j2\sigma_2\sigma_3\rangle \longleftrightarrow |i2\sigma_1\sigma_4, j1\sigma_2\rangle$ . The corresponding matrix elements turn out to be:

$$\begin{aligned} t_1(\sigma, \sigma', \nu) &= 2A_1A_2\widetilde{t_{FM}}(\sigma, \sigma', \nu) + A_1^2\widetilde{t_{MM}}(\sigma, \sigma', \nu), \\ t_2(\sigma, \sigma', \nu) &= [C_2(A_1^2 + B_1^2) + A_1B_1(A_2 + B_2)]\widetilde{t_{FM}}(\sigma, \sigma', \nu) \\ &\quad + A_1(A_1A_2 + B_1C_2)\widetilde{t_{MM}}(\sigma, \sigma', \nu), \\ t_3(\sigma, \sigma', \nu) &= 2(A_1C_2 + B_1B_2)(A_1A_2 + B_1C_2)\widetilde{t_{FM}}(\sigma, \sigma', \nu) \\ &\quad + (A_1C_1 + B_1C_2)^2\widetilde{t_{MM}}(\sigma, \sigma', \nu), \end{aligned}$$

where  $\widetilde{t_{FM}}(\sigma, \sigma', \nu) = \delta_{\sigma\sigma'}\widetilde{t_{FM}}(\sigma, \nu)$ . The procedure followed so far leads to the following effective Hamiltonian:

$$\begin{aligned} H_{eff} &= E_1 \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} + U \sum_{i\sigma < \sigma'} c_{i,\sigma}^\dagger c_{i,\sigma} c_{i,\sigma'}^\dagger c_{i,\sigma'} \\ &\quad - [\sum_{i\sigma\sigma'\nu} c_{i,\sigma}^\dagger c_{i+\nu,\sigma'} \{t_1(\sigma, \sigma', \nu)P_{i0}P_{i+\nu1} \\ &\quad + t_2(\sigma, \sigma', \nu)(P_{i1}P_{i+\nu1} + P_{i0}P_{i+\nu2}) \\ &\quad + t_3(\sigma, \sigma', \nu)P_{i1}P_{i+\nu2}\} + \text{H.c.}], \end{aligned} \quad (11)$$

where  $P_{il}$  is the projector over  $l$  number of particles at the effective site  $i$ . Due to the rapid decay of the hopping terms with distance, in what follows we shall retain only NN effective hopping. At this distance, three hopping amplitudes  $t_j$  can be distinguished for each sum of occupations  $j$ : a) hopping which conserves color ( $\sigma = \sigma'$ ) and the nearest neighbor vector  $\gamma$  lies in the plane  $\sigma$ . We call this amplitude  $t_{jc\parallel}$ , b) same as before with  $\gamma$  at an angle of  $\pi/4$  with the plane  $\sigma$ . We call it  $t_{jc\perp}$ , and c) hopping that does not conserve color ( $t_{jnc}$ ). In this case for a hopping  $\sigma \neq \sigma'$ ,  $\gamma$  must lie in the plane perpendicular to both  $\sigma$  and  $\sigma'$ . The largest of these nine hoppings are the  $t_{jc\parallel}$ . These are the only ones which survive if the electronic structure is approximated as two-dimensional for each  $\sigma$ . For  $\text{Sr}_2\text{FeMoO}_6$  we obtain at the observed lattice parameter:  $t_{1c\parallel} = 0.197$  eV,  $t_{2c\parallel} = 0.179$  eV, and  $t_{3c\parallel} = 0.109$  eV. The next two in decreasing order of magnitude are  $t_{1nc} = 0.075$  eV and  $t_{1c\perp} = 0.047$  eV. The remaining four hoppings lie below 0.03 eV.

#### D. Corrections from excited states

$H_{eff}$  can be systematically improved, including the effects of the states neglected in Subsection B by perturbation theory. The first correction terms are of second order in effective hopping terms. Most of them involve matrix elements of order 0.1 eV or smaller and denominators of order 3eV or larger and can be neglected. The smallest denominator occurs for an intermediate state created by a term similar to  $t_3$ , in which the two-particle eigenstate of  $H_i$  lies  $\simeq 0.3\text{eV}$  above the ground state. However for a non-interacting system, with one electron per site on average, the probability of finding a singly occupied site is  $\simeq 0.1$  and decreases with increasing  $U$ . Then, the effect of this correction on the energy per site is less than 0.01eV and we can also neglect it for fillings around one electron per site.

#### IV. THE SLAVE-BOSON MEAN-FIELD TREATMENT

The formalism used here is essentially a generalization to more than two colors (spin up and down) of the original formulation<sup>12</sup>. The Hubbard model with orbital degeneracy was studied by Hasegawa<sup>29</sup> extending a previous formalism used in the periodic Anderson model<sup>30</sup>, and by Frésard and Kotliar<sup>31</sup>. In our case, the interactions include correlated hopping which does not conserve color. However, the projectors  $P_{il}$  are easily expressed in terms of bosonic operators, and the approximation remains suitable for our problem. The basic idea is to enlarge the Fock space to include bosonic states which correspond to each state in the fermionic description. For example, the vacuum state at site  $i$  is now represented as  $e_i^\dagger |0\rangle$ , where  $e_i^\dagger$  is a bosonic operator corresponding to the empty site; similarly  $s_{i\sigma}^\dagger c_{i\sigma}^\dagger |0\rangle$  represents the simply occupied state with spin  $\sigma$ , and so on. The bosonic operators for doubly and triply occupied states are denoted  $d_{i\sigma\sigma'}^\dagger$  and  $t_i^\dagger$  respectively. In this way the projectors can be expressed in terms of boson operators (for example  $P_{i2} = \sum_{\sigma < \sigma'} d_{i\sigma\sigma'}^\dagger d_{i\sigma\sigma'}$ ) and the interactions between fermions disappear from the Hamiltonian. To restrict the bosonic states to those with a physical meaning, the following constraints must be satisfied:

$$\begin{aligned} e_i^\dagger e_i + \sum_{\sigma} s_{i\sigma}^\dagger s_{i\sigma} + \sum_{\sigma < \sigma'} d_{i\sigma\sigma'}^\dagger d_{i\sigma\sigma'} + t_i^\dagger t_i &= 1 \\ s_{i\sigma}^\dagger s_{i\sigma} + \sum_{\sigma' \neq \sigma} d_{i\sigma\sigma'}^\dagger d_{i\sigma\sigma'} + t_i^\dagger t_i &= c_{i\sigma}^\dagger c_{i\sigma}, \end{aligned} \quad (12)$$

To simplify the notation, we introduce the following operators:

$$\begin{aligned} X_{i\sigma}^\dagger &= R_{i\sigma} s_{i\sigma}^\dagger e_i L_{i\sigma}, \\ Y_{i\sigma\sigma'}^\dagger &= R_{i\sigma} d_{i\sigma\sigma'}^\dagger s_{i\sigma'} L_{i\sigma}, \end{aligned} \quad (13)$$

where

$$\begin{aligned} R_{i,\sigma} &= (1 - e_i^\dagger e_i - \sum_{\sigma' \neq \sigma} s_{i,\sigma'}^\dagger s_{i,\sigma'} - d_{i,\sigma'\sigma''}^\dagger d_{i,\sigma'\sigma''})^{-1/2}, \\ L_{i,\sigma} &= (1 - s_{i,\sigma}^\dagger s_{i,\sigma} - \sum_{\sigma' \neq \sigma} d_{i,\sigma\sigma'}^\dagger d_{i,\sigma\sigma'})^{-1/2}. \end{aligned} \quad (14)$$

with  $\sigma' \neq \sigma \neq \sigma''$ . Inside the expression (13) and using the first constraint (12) these operators are strictly equal to 1. They are introduced to reproduce the correct non-interacting result when the saddle-point approximation is made.<sup>8,29-31</sup> The Hamiltonian takes the form

$$\begin{aligned} \hat{H}_{eff}^{SB} &= E_1 \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} + U \sum_{i\sigma\sigma'} d_{i,\sigma\sigma'}^\dagger d_{i,\sigma\sigma'} \\ &\quad + \sum_{\langle ij \rangle \sigma, \sigma'} \{c_{i\sigma}^\dagger c_{j\sigma'} [t_1(\sigma, \sigma', R_{ij}) X_{i\sigma}^\dagger X_{j\sigma'} + \\ &\quad \sum_{\sigma_1} t_2(\sigma, \sigma', R_{ij}) (X_{i\sigma}^\dagger Y_{j\sigma'\sigma_1} + Y_{i\sigma\sigma_1}^\dagger X_{j\sigma'}) \} \end{aligned} \quad (15)$$

$$+ \sum_{\sigma_1 \sigma_2} t_3(\sigma, \sigma', R_{ij}) Y_{i\sigma\sigma_1}^\dagger Y_{j\sigma'\sigma_2} + \text{H.c.} \} \quad (16)$$

In the saddle-point approximation for the uniform, color-independent solution, all bosonic operators are condensed, *i.e.* replaced by numbers, independent of position and color ( $e_i^\dagger = e$ ,  $s_{i\sigma}^\dagger = s$ ,  $d_{i\sigma\sigma'}^\dagger = d$ ,  $t_i^\dagger = t$ ), and their values are obtained minimizing the energy of the resulting non-interacting fermionic problem under the constraints (12). For one electron per site in the insulating state, one has  $s = 1/3$ ,  $e = d = t = 0$ . In general, for a multicolor problem, the condensates for only one occupation  $n$  are different from zero, and near the metal-insulator transition, the values for  $n - 1$  and  $n + 1$  are infinitesimals of the same order, while the other expectation values of the condensates are infinitesimals of larger order. Thus, using the constraints we can write near the metal-insulator transition:

$$e^2 = 3d^2; s^2 = \frac{1}{3} - 2d^2; t = 0, \quad (17)$$

where  $d \rightarrow 0$ . The stability with respect to  $d$  determines the position of the metal-insulator transition. Specifically, replacing (17) in (16) the energy up to order  $d^2$  takes the form

$$E(d) = E_1 + (3U + E_{TB})d^2 \quad (18)$$

where  $E_{TB}$  is the energy of a tight-binding Hamiltonian in the f.c.c. lattice, in which the three different NN hopping amplitudes  $T_\xi$  (denoted by the subscripts  $\xi = c \parallel$ ,  $c \perp$  or  $nc$  are described as before) are weighted averages of the  $t_{i\xi}$ :

$$T_\xi = t_{1\xi} + \frac{4\sqrt{3}}{3}t_{2\xi} + \frac{4}{3}t_{3\xi} \quad (19)$$

Clearly, the transition is at the point  $U = -E_{TB}/3$ , and for the case in which the hoppings do not depend on the occupancy of the sites involved, previous results are recovered.<sup>29,31</sup> We have calculated  $E_{TB}$  using a mesh of 286 points in  $1/48$  of the Brillouin zone of the f.c.c. lattice. The values of  $t_{i\xi}$  and  $U$  were calculated as described in the previous section, and we have looked for the value of  $\varepsilon_{Mo} - \varepsilon_{Fe}$  (the most uncertain parameter of the original Hamiltonian) at which the metal-insulator transition takes place. The result as a function of pressure is represented in Fig. 3. In the same figure we show the value of  $\varepsilon_{Mo} - \varepsilon_{Fe}$  for  $\text{Sr}_2\text{FeMoO}_6$  derived as explained in Section II from *ab initio* calculations. If for a given pressure this *ab initio* value lies below the metal-insulator boundary obtained with the SBMFA, the system is predicted to be a metal. In the opposite case, the mobility of the carriers is strongly reduced as a consequence of the electronic correlations and an insulating behavior is expected. We actually see that  $\text{Sr}_2\text{FeMoO}_6$  is very near a metal-insulator transition and that negative pressure can drive it insulating, mainly due to reduction of the hopping amplitudes as the lattice parameter is expanded. This might be the

main reason of the insulating character of  $\text{Sr}_2\text{FeWO}_6$ . In our formalism, in the insulating phase, the occupation at Fe is given by  $A_1^2$ . This value at the transition is 0.97 and should decrease further when delocalization effects, not adequately taken into account by the SBMFA, are included. Then, one expects an oxidation state near +2 for Fe in the insulating state, but not exactly  $\text{Fe}^{+2}$ . Similarly, the magnetic moment at Fe sites is slightly above  $4\mu_B$ , and that of Mo slightly below zero. Covalency with O atoms, modifies these values, particularly the valence.<sup>8</sup>

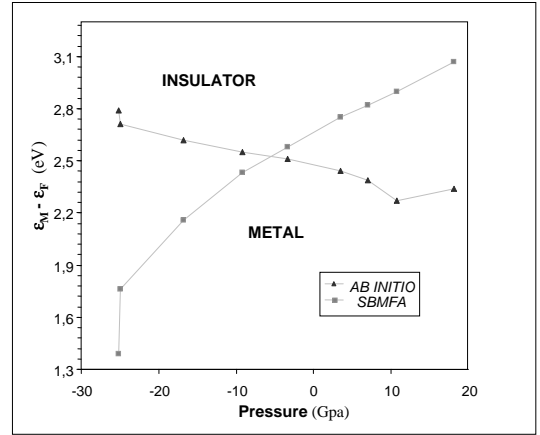


Fig. 3

FIG. 3. Full line: phase diagram for the metal-insulator transition as a function of  $\varepsilon_{Mo} - \varepsilon_{Fe}$  and pressure. Dashed line: values of  $\varepsilon_{Mo} - \varepsilon_{Fe}$  for  $\text{Sr}_2\text{FeMoO}_6$ , obtained using the *ab initio* results of Table I.

## V. SUMMARY AND DISCUSSION

Starting from a model describing transition-metal  $t_{2g}$  orbitals in half-metallic double perovskites like  $\text{Sr}_2\text{FeMoO}_6$ , and assuming that on-site Coulomb interactions are important in only one of the transition-metal ions (Fe), we have derived an effective Hamiltonian  $H_{eff}$ , which contains only one species of effective atoms in an

f.c.c. lattice with moderate on-site interaction. This seems to be the maximum possible reduction of the relevant Hilbert space per unit cell, and we expect that it can be useful for future studies in similar systems in which correlations are explicitly taken into account. As long as the difference in bare on-site energies (in contrast to the Hartree-Fock or *ab initio* ones) is not very small, the interactions in  $H_{eff}$  are important and some treatment which appropriately takes into account many-body effects is necessary for its study. Our derivation can be generalized to include both spins. However, our formalism is not appropriate to treat the case of disorder systems in which the highly correlated transition metal can occupy both sublattices.<sup>32</sup> For an occupation near one  $t_{2g}$  minority electron per unit cell,  $H_{eff}$  is very accurate. If the occupation is near two electrons per site, our calculations should be extended to include states with three electrons per unit cell, and perturbative corrections due to neglected excited states in the two particle sector.

We have applied  $H_{eff}$  to analyze the metal-insulator transition as a function of pressure or  $\varepsilon_{Mo} - \varepsilon_{Fe}$  in  $Sr_2FeMoO_6$ . While a similar study was previously done,<sup>8</sup> the accuracy of the present results should be higher because the highest energy involved in the problem ( $U_{Fe} \simeq 7\text{eV}$ ) and most of the Fe-Mo hopping, is treated exactly in  $H_{eff}$ . We obtain that the region of insulating behavior increases with respect to the previous calculation, and a metal-insulator transition is predicted for a negative pressure near -5 GPa.. Although we do not know the parameters of the starting model for  $Sr_2FeWO_6$ , we believe that the insulating character of the compound,<sup>4</sup> or the alloys  $Sr_2FeW_xMo_{1-x}O_6$  for  $x \simeq 1$  is related with this transition.  $\varepsilon_W - \varepsilon_{Fe}$  is expected to be higher than  $\varepsilon_{Mo} - \varepsilon_{Fe}$  due to the larger W-O hopping.<sup>7</sup> Actually for  $x = 1$ , the system is antiferromagnetic and our  $H_{eff}$  derived here does include both spins. However, we believe that the difference in energy between ferro- and antiferromagnetic insulating phases is due to double exchange interactions which are smaller than the energetic ingredients, whose competition determines the metal-insulator transition. In simple terms, in the metallic state, ferromagnetism is favored by energies of the order of the effective  $t_j \sim 0.2\text{ eV}$  (similarly to other proposals<sup>7,33</sup>), while in the insulating state, antiferromagnetism is favored by energies of order  $t_j^2/U \sim 0.01\text{ eV}$ . The situation is similar to the metal-insulator transition which takes place in  $RNiO_3$  replacing rare earths  $R$  or changing temperature.<sup>34</sup> It seems that the antiferromagnetic order does not affect the metal-insulator transition, and the boundary between metal and paramagnetic or antiferromagnetic order is continuous and smooth. In the starting Hamiltonian we have assumed that the O atom lies in between its two NN transition-metal (TM) ions. If this is not the case, as suggested by some structural measurements<sup>35</sup> an increase in lattice parameter might increase the effective hopping between TM atoms (for example by a reduction of the TM-O-TM angle, as in  $RNiO_3$ <sup>34</sup>). This might be the reason  $Ba_2FeMoO_6$  is still

metallic in spite of the increase in the distance between TM atoms.

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## APPENDIX A: EVALUATION OF THE SUMS $S$

Here we describe the evaluation of the sums  $S(\eta) = \sum_{\Delta_\sigma} C_\sigma(\Delta_\sigma) C_{\sigma'}(\Delta_{\sigma'})$ , with  $\Delta_{\sigma'} - \Delta_\sigma = \eta$  and  $\sigma \neq \sigma'$ . For the sake of clarity, we assume  $\sigma = xy$  and  $\sigma' = zx$ . The other cases are easily obtained using symmetry arguments. We can then write:

$$\begin{aligned} \eta &= \frac{a}{2}(n_x \hat{x} + n_y \hat{y} + n_z \hat{z}); \Delta_{xy} = \frac{a}{2}(n'_x \hat{x} - n_y \hat{y}); \\ \Delta_{zx} &= \frac{a}{2}[(n'_x + n_x) \hat{x} + n_z \hat{z}], \end{aligned} \quad (A1)$$

where  $n_x$ ,  $n'_x$ ,  $n_y$ , and  $n_z$  are integers with  $n_x + n_y + n_z$  even and  $n'_x + n_y$  odd ( $\eta$  is a vector of the f.c.c. lattice, but  $\Delta_\sigma$  and  $\Delta_{\sigma'}$  are not). Using the definition of  $\Delta_\sigma$  (Eq.(2)), we can write:

$$S = \sum_{n'_x} \frac{1}{N_{xy} N_{yz}} \sum_{k_x, k_y, k'_x, k'_z} \exp[i \frac{a}{2} (-k_x n'_x + k_y n_y + k'_x (n'_x + n_x) + k'_z n_z)]. \quad (A2)$$

We can assume that the system is a cube of edge  $L$ , and then the number of atoms lying in the plane  $\sigma$  is  $N_\sigma = 2(L/a)^2$ . The sums over the two dimensional wave vectors  $k$  and  $k'$  run over a square Brillouin zone with sides of length  $2\sqrt{2}\pi/a$  rotated  $\pi/4$  with respect to  $\hat{x}$ . Depending on the parity of  $n_y$ , the sum over  $n'_x$  runs either over all odd values or over all even values, and:

$$\sum_{n'_x} \exp[i \frac{a}{2} n'_x (k'_x - k_x)] = \frac{L}{a} [\delta_{k_x, k'_x} - (-1)^{n_y} \delta_{k_x, k'_x + 2\pi/a}]. \quad (A3)$$

Using this expression to eliminate the sum over  $k_x$  in Eq. (A2), and replacing the remaining sums by integrals in reciprocal space, one obtains:

$$\begin{aligned} S(\eta) &= \frac{a^3}{4\pi^3} \int_0^{2\pi/a} dk'_x \cos(k'_x n_x) \int_0^{2\pi/a - k'_x} dk'_z \cos(k'_z n_z) \\ &\times [\int_0^{2\pi/a - k'_x} dk_y \cos(k_y n_y) \\ &- (-1)^{n_y} \int_0^{k'_x} dk_y \cos(k_y n_y)]. \end{aligned} \quad (A4)$$

The integrals are elementary and after some algebra, the result becomes:

$$S\left(\frac{a}{2}(n_x\hat{\mathbf{x}} + n_y\hat{\mathbf{y}} + n_z\hat{\mathbf{z}})\right) = \frac{(-1)^{n_x}}{\pi^2 n_y n_z} (\delta_{n_x+n_y-n_z,0} + \delta_{n_x-n_y+n_z,0} - \delta_{n_x+n_y+n_z,0} - \delta_{-n_x+n_y+n_z,0}). \quad (\text{A5})$$

This expression and Eqs (6) and (7), allow to calculate all hopping terms in the new basis.

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